

M. Herman

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(71) Applicant: Müller, Michaela, 66121 Saarbrücken, DE	(72) Inventor: Same as applicant
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(54) **Mineral Mixture for the Preparation of Foamed Building Materials, Insulating Materials, and Structural Components**

(57) The invention relates to the preparation of foamed mineral structures for the production of molded articles of any shape for use as building and insulating materials or of foamed structures, which are applied to existing substrates or fill existing articles. To improve their properties, the molded pieces and structures can be reinforced by incorporated reinforcing and/or bearing parts.

The foamed articles and structures are prepared by reacting ground oxide mixtures of calcium, silicon, and aluminum, and/or magnesium with aqueous solutions of alkali silicates, the so-called water glasses. The employed oxide mixtures arise as by-products in smelting processes as slag or in sintering processes as so-called clinker.

To achieve the foam structure, air or a propellant gas is mixed into the mixtures or a propellant gas is produced in situ by chemical reaction with gas-releasing materials.

The mixtures capable of foaming can contain generally known inorganic or organic fillers, paint pigments, and if appropriate, additives to improve structure and processing.

The foamed articles or structures harden within a short time at ambient temperatures without an additional energy supply. The hardened articles are mechanically exceptionally stable and can be easily processed further.

They [can be used] as noncombustible insulating building materials for protection from heat, cold, and noise, as decorative ...

Specification

The invention relates to mineral foam structures, which foam by simple mixing together a finely ground material mixture comprising oxides of silicon, calcium, aluminum, and/or magnesium with water-soluble alkali silicates, so-called water glasses, if appropriate, with addition of inert mineral fillers, and additives and propellants, known per se, after placement in molds or after application with suitable application devices onto substrates and harden into foamed articles with a high strength without addition of external energy.

It is prior in the art to produce foamed molded articles from alkali silicates as binders (so-called water glasses), suitable hardening agents for these alkali silicates, and possibly inorganic fillers.

A system is described in German patent No. 21 10 059, in which a water glass, modified with triglycidil isocyanurate, amines, and a quaternary ammonium base, was foamed with addition of fillers, a mixture of calcium phosphate and sodium silicofluoride as the hardening agents and H_2O_2 , a perborate, or with aluminum powder as the propellant and after tempering for several hours was hardened into stable molded articles.

This system is not comparable with the system according to the teaching of the claimed invention. It requires costly organic stabilization for the employed alkali silicate, a hazardous hardening component, and a costly subsequent treatment to be able to produce stable foam structures thereby. The volume increase through foaming is low and the necessary hardening time of 2 h, without the necessary subsequent tempering, is very long.

Systems are described in the French patent applications No. 79 22 041 and No. 80 18 970, which are based on combinations of aqueous solutions of alkali silicates and alkali lyes with a special aluminum silicate, the so-called metakaolin. These systems can also be foamed by addition of propellants.

In so doing, very specific molar ratios of the employed reactive ingredients must be maintained. According to this prior art, the so-called metakaolin—a reactive aluminosilicate, which is obtained by tempering kaolinite to 800°C —is the active component which leads to the formation of a macromolecular aluminosilicate structure. Metakaolin is also the sole reactive solid component of these systems, apart from the possibly used inert fillers.

The molding compounds according to this invention are moreover very costly and difficult to handle. After mixing of the starting materials, they require considerable prereaction time (= maturing time) before the actual processing. Moreover, they must be subjected to an additional heat treatment for hardening.

Furthermore, only one metakaolin produced from kaolinite with a very specific provenance and modified by additional temperature treatment (and thus expensive) can be used for its preparation. Finally, no foam structures producible by injection/spraying can be produced by the systems according to this prior art.

Finally, foamable, water-containing hardenable molding compounds, based on aqueous alkali silicate solutions, SiO_2 , and fillers, are described in DE patent No. 32 46 619; these are characterized in that they contain oxide mixtures of extremely finely divided amorphous SiO_2 and possibly aluminum oxide as the major reactive components, which form as dust, free of water, in high-temperature smelting processes from the vapor or gas phase.

Such substances are known to one skilled in the art as so-called filter dusts. They can accumulate, e.g., in ferrosilicon production. However, the necessary SiO_2 can also be introduced into the systems, if appropriate, by means of precipitated silicic acid (silica gel).

The specific surface area of these substances (measured according to BET) is about 18–22 m^2 (equivalent to 180,000–220,000 cm^2/g).

These known systems according to this prior art are also not comparable with the claimed invention.

They stem exclusively from raw materials having a totally different structure and origin and use explicitly only extremely finely divided, reactive, amorphous SiO_2 , possibly together with likewise finely divided aluminum oxide as the components reactive with the alkali silicate/alkali hydroxide mixture. In this case, special value is placed on the presence of extremely finely divided amorphous silicon dioxide, as it accumulates as filter dust from the gas phase/vapor phase, e.g., in metallurgical processes. This amorphous SiO_2 is the principal carrier of the reaction according to this invention.

During hardening of the system as taught by this invention, the amorphous silicon dioxide is brought into solution through the highly alkaline alkali silicate component or at least solubilized, and polysilicates arise by reacting under these conditions, if necessary with co-reaction of present aluminum oxides, which apparently serve as network modifiers here but are not absolutely necessary according to the teaching of this invention.

In contrast, the system according to the claimed invention derives explicitly from a three-material mixture of oxides of silicon, calcium, aluminum, and/or magnesium. The employed material mixtures originate from by-products solidifying glass-like in the melt in high-temperature processes. They are typically designated as slag and accumulate, e.g., in the

smelting of metals, or are products produced by sintering processes, e.g., "clinker." Such "clinker" arises, e.g., as the raw product in cement production in a rotary tube furnace.

For use as a component of systems according to the teaching of this invention, these substances must be ground to a suitable fineness in a known manner. The necessary grinding fineness is at least of the magnitude also typical for the production of conventional cement, thus in the range of a specific surface area of about 2000 to 4500 cm²/g (0.2 to 0.45 m²) according to Blaine. A grinding fineness above 3500 cm²/g according to Blaine is preferred, and fineness values above 3900 cm²/g are especially preferred.

The objects of the claimed invention are thus mineral foam systems, arising from the reaction of aqueous solutions of alkali silicates with material mixtures of oxides of silicon, calcium, aluminum, and if appropriate magnesium, which arise as by-products or main products during high-temperature smelting or sintering processes.

Known species of this material mixture are slags from silicate melts, preferably the so-called blast-furnace slag, as they arise, e.g., in the smelting of metals and which, e.g., are also used for the preparation of so-called slag cements, blast-furnace cements, iron portland cement, and sulfate slag cements.

The material mixtures, which can be used for the claimed invention, include furthermore so-called fused basalt, aluminous cement, the high-alumina cement produced by sintering (as "clinker"), and brick meal, preferably those from calcining processes under 1000°C.

Certain slags from coal and coke firing, e.g., also from melting chamber firings of power plants, also contain material mixtures of the described oxides and are suitable, if appropriate after minor modification, for the production of the mineral foam articles of the claimed invention.

These substances are known from the literature. An extensive description of these species of substances, which may be used as reactive components for the mineral foam system according to the claimed invention, can be found in "Keil: Hochofenschlacke" [Keil: Blast-furnace Slag], Verlag Stahleisen, Düsseldorf, 1963, and "Hinze: Silikate. Grundlagen der Silikatwissenschaft" [Hinze: Silicates. Fundamentals of Silicate Science], Vols 1+2, VEB-Verlag Bauwesen, Berlin, 1971, and in the literature references cited therein.

According to the claim of the invention, highly alkaline aqueous solutions of alkali water glass—the so-called water glasses—are used as the liquid alkali silicates. These water glasses are generally known and described at length and comprehensively in the literature. A short, yet precise description can be found, e.g., in "Engler: Lösliche Silikate" [Engler: Soluble Silicates] in

Seifen-Fette-Öle-Wachse, 1974, No. 8 ff., Verlag Ziolkowski, Augsburg, and in the literature cited therein.

For systems according to the claimed invention, alkali silicate solutions with an average to low viscosity and a high proportion of alkali hydroxide ($\text{pH} > 11.5$) are preferred.

It was surprising that a mineral foam hardening very rapidly at room temperature and having a very high final strength can be produced by smooth reaction of a ground blast-furnace slag having the approximate composition

SiO_2 37 parts by weight

Al_2O_3 16 parts by weight

CaO 32 parts by weight

Other oxides 13 parts by weight

with a Blaine value of only $4000 \text{ cm}^2/\text{g}$ (thus a material that is 50 times coarser than filter dust) and 70% by weight of an aqueous solution of alkali silicate having a molar ratio of 1.48 and 25.6% SiO_2 with addition of typical propellants.

A high-alumina cement, ground to about $4000 \text{ cm}^2/\text{g}$ according to Blaine, having a proportion of

SiO_2 7%

CaO 40%

Al_2O_3 49%

can be reacted to a high-strength mineral foam in a similarly smooth reaction with about 70% by weight, based on the total solids, of an alkaline alkali silicate having a molar ratio of 1.48 in aqueous solution, and 25.6% SiO_2 with addition of propellants. When oxide mixtures arising by sintering such as the described high-alumina cement are used, it is efficient to blend the total system, in order to stabilize it, with admixed inert fillers—for example, by mineral powders such as ground basalt, ground quartz, or ground limestone.

The precise mineralogical structure of the artificial inorganic substance formed during the formation reaction according to the claim of the invention could not yet be explained precisely.

According to the already cited literature, however, it must be assumed that calcium aluminosilicate structures form preferentially during the reaction of the oxide mixture with the alkali silicate in solution; during the formation of said silicates, the alkali hydroxides of the alkali silicates function initially as activators and if appropriate act further on the glassy SiO_2 of the material mixture and integrate it into the reaction so that CaO acts additionally as a network

modifier and through exothermic reaction furthermore assumes the role of an accelerant for the entire reaction.

As propellants for the production of the foam structure, substances can be admixed, which liberate gases by reacting with the alkaline milieu. Suitable are, e.g., inorganic peroxides, such as sodium percarbonate or sodium perborate, hydrogen peroxide, silicon powder, or aluminum powder. The breakdown of the peroxides can be accelerated by certain metal oxides/salts, such as, e.g., manganese oxide or potassium permanganate, so that the foaming behavior of the material mixtures can be adjusted very precisely. The propellants are used preferably in amounts between 0.05 and 5%, based on the total material mixture.

The mineral foam systems according to the claimed invention can contain in addition typical pigments or mineral fillers, such as are generally very well-known from the chemistry of paints, surface coatings, plasters, mortar compounds, thus usually finely ground or appropriately sintered unrefined mineral powders, or also granules.

Reinforcing fillers, such as, e.g., the various mica and other layered silicates, wollastonite, and mineral mixtures known under the names Plastorit, Sillitin, and Micaplast are especially suitable as fillers. Organic fillers are also suitable as loading material, but are not preferred.

Light fillers, such as, e.g., blown perlite and vermiculite, granules of foamed glass, hollow microspheres made of glass and ceramic, and similar known materials can be admixed to the mineral foam, according to the claimed invention, to increase the volume and if appropriate to improve further the heat insulating properties.

To improve structural strength—particularly in foams with a low volumetric weight—reinforcing fibers made of glass, basalt, slag wool, aluminum oxide, asbestos, and also fibers made of cellulose and organic polymers can be mixed with the material mixture. Fibers that are not attacked by the high alkalinity of the material mixture are preferred.

To regulate the cell structure of the mineral foams according to the claimed invention, both rheological aids known from the chemistry of surface coatings, paints, plasters, and mortar compounds can be used—examples are the various hydroxycelluloses but also other alkali-stable polysaccharides, polyacrylates, and surfactants, such as, e.g., quaternary ammonium compounds. Compounds employed, e.g., in the production of foamed concrete or PUR-polyether foams, such as, e.g., protein hydrolysates and water-soluble silicone surfactants can also be used.

Alkyl silanes but also liquefiers, as they are known from cement chemistry, can be used advantageously to regulate the flow behavior of the mineral foam systems as taught by the invention.

The person skilled in the art is familiar with these additives and their mode of action. He also knows that these additives, because of their high activity, need to be used in only small amounts to achieve the desired effect. In practice, the total proportion of additives does not exceed the total amount of 0.5–5%, so that the nature of the invention as an inorganic, mineral system is not adulterated by these—which are organic substances in virtually every case.

Suitable pigments, fillers, fibers, and additives for the systems as taught by this invention are described at length, e.g., in "Kittel: Lehrbuch der Lacke und Beschichtungen" [Kittel: Handbook of Lacquers, Varnishes, and Coatings], Vol. II+III, Verlag Colomb, Berlin-Oberschwandorf, 1974.

The material mixtures from the individual components of the mineral foam system according to the claim of this invention can be prepared by mixing the individual formulation components in any sequence. In practice, one proceeds such that a two-component system is prepared from the solids and the liquid components or—in an execution according to claim 2—the alkali silicate component is added in dry form also to the dry mixture.

For processing, both components are then thoroughly combined, or in the case of an execution according to claim 2, the dry mixture is mixed with an appropriate amount of water similar to mortar. In this case, additives available in liquid form are added to the mixing water.

All typical mixing apparatus for dry-liquid mixtures can be employed for mixing. Large amounts are expediently prepared with automatic metering machines.

Molded articles of any geometry can be made from the mineral foam system according to claim of the invention. Thus, insulating boards for heat and noise insulation can be prepared, support plates for decorative coatings made of other materials, channel systems for ventilation ducts and electrical lines, e.g., for fireproofing, light partitioning structures, core plates for sandwich structures, and composite elements, molded parts for housings for blinds, heat-insulating and light-weight lintels for windows and doors, shells for pipe insulation, to name only a few of the possible applications of articles made from the mineral foam systems according to the claim of this invention. If necessary, the molded articles can be reinforced with embedded reinforcement made of nonwovens, fabrics, metals, etc.

Because the mineral foam adjusts to any shape, it is also possible to fill already existing hollow molded pieces made of other materials and thereby to insulate or strengthen at a later time.

With sprayable materials based on the described systems according to the claimed invention, it is also possible to fill hollow spaces, e.g., in mining and the building of tunnels, or to apply so-called position foam insulation directly in the main part of a building.

For all these applications, it is especially advantageous that the mineral foam systems according to the claim of this invention harden totally without application of any external energy within a short time—adjustable from a few minutes to 2–3 h—and thus short cycle times are possible particularly in industrial fabrication.

Examples

Example 1

100 parts of a material mixture, consisting of 37.86% ground slag, containing 36.50% SiO_2 , 42% CaO , 12% Al_2O_3 , and 7.5% MgO (Blaine value of 4300), 2.23% CaOH , 4.45% Sillitina Z 86, 4.45% ground basalt, 0.11% aluminum powder, 0.67% sodium percarbonate, and 0.11% potassium permanganate, were combined with 13.36% foamed glass granules having a grain size of 1–2 mm, and 39.98% of an aqueous alkali silicate solution having a molar ratio of 1.48 and a SiO_2 content of 25.6%, and poured into a cube-shaped mold. Temperature 20°C.

The substance began to foam after about a minute. After about 20 min, foaming ended and the foamed article had solidified so extensively that the resulting cube of mineral foam with additional light filler could be removed and cautiously transported. After about 2 h, the article had hardened totally and could be processed.

The resulting foam structure was closed-celled; the average foam pore diameter was about 1.5 mm. After 72 h of storage at room temperature, the article was subjected to a fire test. The foam structure was heat-resistant to about 1000°C.

Example 2

100 parts of a material mixture, consisting of 43.15% ground slag, containing 36.50% SiO_2 , 42% CaO , 12% Al_2O_3 , and 7.5% MgO (Blaine value of 4300), 2.54% CaOH , 6.35% mica, 2.54% kaolin, 0.13% aluminum powder, 0.76% sodium percarbonate, and 0.13% potassium permanganate, were combined with 44.42% of an aqueous alkali silicate solution having an

alkali content of 27% and a SiO_2 content of 29.5%, and containing a silicon surfactant, and poured into a cube-shaped mold. Temperature 20°C.

The substance began to foam after about a minute. After about 12 min, foaming ended and the foamed article had solidified so extensively that the resulting cube of mineral foam with addition light filler could be removed and cautiously transported. After about 120 min, the article had hardened totally and could be processed.

The resulting foam structure was closed-celled; the average foam pore diameter was about 0.5 mm. After 72 h of storage at room temperature, the article was subjected to a fire test. The foam structure was heat-resistant to about 1200°C.

The examples are exemplary of many of the possible execution variants of mineral foam structures/foamed articles according to the claim of this invention. They are thus only typical examples.

Any person skilled in the art is capable of producing similar foamed structures with the information provided as taught by this invention on the basis of the typical novel parameters—reaction of oxide mixtures of calcium, silicon, and aluminum, which originated from smelting or sintering processes and are ground sufficiently fine, with aqueous solutions of alkaline alkali silicates, with addition of propellants and if appropriate additives and fillers.

These possible variations of the invention are also claimed from the described invention.

Claims

1. Mineral, hardenable foam structures (mineral foams) and structural components, molded articles, and position foams, produced therefrom, by reacting oxides of silicon, calcium, aluminum, and/or magnesium with aqueous solutions of alkali silicates, if appropriate, with addition of inert fillers, propellants, and additives, **characterized in that** the foam system contains 2 to 70% oxides, which accumulate as the main or by-products from high-temperature smelting and sintering processes, and may already be available as a material mixture, and aqueous solutions of alkali silicates, the so-called water glasses.
2. Mineral foams according to claim 1, characterized in that the reaction mixture may contain in addition hardening substances, known per se, for alkali silicate solutions, which may act as reaction accelerators and co-hardeners for the system. Examples of such substances are polymeric (condensed) phosphates of aluminum. Such hardener systems for alkali silicates are described, for example, in DE patent No. 27 09 189.

3. Process for the preparation of the foam system according to claims 1 and 2, characterized in that the alkali silicate necessary for the reaction is mixed into the material mixture also as dry substance readily soluble in water (so-called hydrated water glass) with a residual water content between 8 and 20%, based on the solid, the alkali hydroxides necessary to adjust the $\text{Me}_2\text{O}:\text{SiO}_2$ ratio are also added dry to the material mixture, and the dry mixture can be mixed with pure water to prepare a processable mass.
4. Process according to claims 1 to 3, characterized in that the volumetric weight (density) of the produced foam structure can be varied by means of simply changing the amount of propellant and if appropriate the other added additives and fillers over broad ranges between about 50 kg and 1200 kg per cubic meter.
5. Process according to claims 1 to 4, characterized in that the foamed structure can be hardened to a hard, exceptionally stable article without addition of external temperature—thus at an ambient temperature.
6. Process for the preparation of molded articles of any geometry from the foam system according to claims 1 to 5, characterized in that a flowable or still malleable mass is prepared from the oxide mixtures, aqueous solutions of the alkali silicates, or (with preparation of the material mixture according to claim 3) with water and if appropriate additives and foaming agents and foamed in molds for shaping.
7. Process according to claims 1 to 6, characterized in that the foam system can be applied without molding by machine directly to a substrate or into a shape—for example, by injection or spraying.
8. Process according to claims 1 to 7, characterized in that structures can be prepared according to claims 6 to 7 from the foam system according to claims 1 to 5 by incorporated preformed reinforcement of fiber structures of any type, for example, by fabric and nonwovens made of glass, synthetic fiber, or metal, or by reinforcements made of steel similar to reinforcement technology in steel concrete, and statically bearing structural components can also be prepared from the thus reinforced shaped articles.
9. Foam systems and shaped pieces therefrom according to claims 1 to 8, characterized in that they can be worked with conventional tools as are typical for woodworking, metalworking, and stone working, e.g., by drilling, milling, and sawing.
10. Construction materials, insulating materials, and structural components prepared from foam systems according to claims 1 to 9.